

FINAL REPORT ON THE USE OF
REINFORCED INORGANIC
CEMENT MATERIALS FOR
SPARK WIRE AND
DRIFT CHAMBER WIRE FRAMES

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PREPARED BY:
MEGA ENGINEERING
10230 NEW HAMPSHIRE AVENUE
SILVER SPRING, MARYLAND 20903

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PROJECT SUMMARY
EVALUATION OF GLASS FIBER REINFORCED CEMENT FOR
SPARK WIRE AND DRIFT CHAMBER WIRE FRAMES

The purpose for this research was to evaluate the feasibility of using glass fiber reinforced in-organic cement (GFRC) for fabricating large dimensioned (ie., 1 meter and larger) structural frames for supporting a number of precisely located spark wires in multiple planes. These frames have applications for space qualified spark chamber wire frames and drift chamber wire frames.

As part of this research, a survey of the current "state-of-the-art" in glass fiber reinforced cement materials was made; calcium aluminate material sample mixes were made and tested to determine their laboratory performances. Tests were conducted on both commercially available sample materials and new material mixes. The results of these tests showed that compressive and flexural strengths of this material could approach those values which would enable fabrication of structural spark wire frames for space applications. The results of this SBIR investigation developed the following conclusions and recommendations:

1. The use of calcium aluminate glass fiber reinforced cement presents a potential for improving the fabricability of large spark wire and drift chamber frames. The material properties reported in the literature would indicate that the properties approach the strengths of some of the ceramic materials previously used without the fracture sensitivity of those ceramics.
2. The use of glass reinforced calcium aluminate should produce flexural strengths well in excess of 10,000 psi and probably close to 15000 psi minimum. However, the limited number of tests conducted as part of the current SBIR research showed nominal flexural modulus of rupture strengths between 5000 to 8000 psi depending on the mixes, reinforcing and water to cement ratios used. Additional samples with various mixes and cure temperatures are needed to verify potentially higher strengths.
3. There is also a need to evaluate the long term creep and long term strength degradation properties of the current commercial treated glass fiber materials used with calcium aluminate materials available.
4. There is a need to develop an assembly procedure specifically for the spark wire frame fabrication using a "spray-Up" system and de-watering system to evaluate the problems associated with this process.

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EVALUATION OF GLASS FIBER REINFORCED CEMENT FOR SPARK WIRE AND DRIFT CHAMBER WIRE FRAMES

1.0 Introduction

This report presents the results of a survey, materials test and analysis study directed toward the development of an inorganic glass-fiber reinforced cement material for use in the construction of space qualified spark wire frames and drift chamber frames. The purpose for this research was to evaluate the feasibility of using glass fiber reinforced cement (GFRC) for large dimensioned (ie., 1 meter and larger) structural frames for supporting a number of precisely located spark wires in multiple planes.

As part of this research, a survey of the current "state-of-the art" in fiber reinforced cement materials was made; material sample mixes were made and tested to determine their laboratory performances. Tests conducted on sample materials showed that compressive and flexural strengths of this material could approach values which would enable fabrication of structural spark wire frames.

1.2 Project Background

Currently, large spark wire frames and drift chamber frames for space applications must be fabricated from machined ceramic materials or machined and molded fiberglass materials. Both of which present major limitations for spark wire and drift chamber fabrications. For example, previously designed frames for the Energetic Gamma Ray Telescope (EGRET) spark chamber utilized a Corning Glass companies' ceramic MACOR material which was machined from extruded "logs" into flat beams and then these were bonded together to form a "picture frame structural frame for support of wire planes. Previous spark chamber frames were made in a similar way. For example, the SAS-B spark chamber telescope and other balloon launched spark chamber frames utilized glass bonded mica frames. These frames used a ceramic material formed of a glass matrix and a mica flake filler. Both of these frames and their materials suffered from the problems of brittle fracture and creep which degraded the structural performance of their materials under the wire plane loads and launch environment forces.

All of these previous frame materials were extremely brittle and notch sensitive. Surface finishes had to be carefully polished to minimize surface flaws. Ground based spark wire frames such as those made at the Brookhaven National Laboratory were fabricated primarily from fiberglass materials. However, since this material utilizes epoxies as a glass matrix, the

organic compound polymers in the fiberglass epoxy resins can produce problems with contamination of the ionizing gas within these detectors. The result is that the chamber gas must be replenished more frequently than with an inorganic frame material.

1.3 The Current Project's Research Objectives

The objectives of the present SBIR phase-I study was to verify the potential use of GFRC for space applications and in particular for wire frame structures. It was the intent of this research to demonstrate that an appropriate GFRC mix could provide the necessary structural properties required to accomplish the following:

- Minimize brittle fracture by arresting crack propagations by: internal fiber reinforcement interfaces, inert granular interfaces and residual voids which would blunt a crack tip.
- Provide a castable and or "spray" up fabrication method which would permit molding or forming wire frame structural members with minimal tooling and limited or no machining.
- Provide an in-organic environment for spark gas which would eliminate the need for frequent replenishment of the gas within a chamber.
- Provide a material with very high compressive strength natural to the cement matrix and an improved tensile strength developed by means of its suitable reinforcement fibers.
- Provide a material which can be controlled to produce desired directional properties by orienting the fiber volume and orientation of the fiber reinforcements used.
- By using refractory cements, relatively high strengths at high temperatures would assure structural integrity for welding and soldering wires to the frame.

Most of these requirements have been verified as part of this present SBIR research project, either through extensive reviews of existing research results or through actual laboratory tests conducted on candidate materials.

2.0 Candidate Materials Selected for Evaluation:

The present research project has concentrated primarily on inorganic hydraulic setting cements. Typical types of cements include¹:

- Portland cement
- Calcium Aluminate (High Alumina or Aluminous) cement
- Pozzolanic Cement
- Slag and other natural cements

2.1 Problems with In-Organic Cements

Inorganic materials like cements and gypsum are strong in compression but are comparatively weak in tension². Although brittle themselves, these binders can provide suitable matrices for fiber reinforcement. Therefore, if the composite material is properly mixed and properly cured relatively high allowable tensile and flexural stress levels can be achieved³.

Commercially available glass fibers can be used to reinforce various cement mixes in order to produce improved tensile strength and improved impact properties suitable for aerospace structural uses⁴. The resulting properties will depend upon the mixes, water content and the glass percentages used in the mix.

Some research has shown, however, that the tensile performance may degrade with time if provisions are not made to reduce the alkalinity of the cement matrix used⁵.

2.2 Reasons for Selecting Calcium Aluminate Cement

The present study concentrated on the evaluation of calcium aluminate "refractory type cements" primarily because this material has a strength of over twice that of the more common portland cement⁶. It is also more resistant to high temperatures and to attack by sulfates and water than portland cement. It also develops optimal strength at relatively high water/cement ratios thus giving it a very workable mix which is quite important when using "spray-up" fabrication methods.

One of the most practical reasons for using Calcium Aluminate is its relatively low alkalinity environment which would tend to degrade glass fibers less than portland cement materials-

The strength of calcium aluminate cement is critically

dependent upon its temperature in curing⁸. Excessive temperature used in curing will degrade the strength and low temperatures will result in larger crystalline structures which produce lower strengths.

Figure 1 below shows the approximate composition for each of these types of cements. The primary strength developed in the calcium aluminate type cement is a function of the complete hydration of calcium aluminate and ferrites. Reference 9 provides a review of the research progress in evaluation of this hydration mechanism. Proper hydration of CA is strongly dependent upon the cure temperature and the types of filler materials used. The formation of small crystal structures at the filler boundaries under proper cure temperatures will improve the strength of the cement mix. The effects of temperature on the hydration of calcium aluminate cement are described by Rettel et al¹⁰.

The effects of elevated temperature heating of calcium aluminate was investigated by Puertas and Trevino and Bachiorrin-ll to follow the crystallization and polymorphism of CA during heating up to temperatures of 100° C.

Calcium Aluminate (CA) cements have been successfully used for many years for electrical insulators, electrical dielectric spacers, thermal insulators and electrical supports for various applications. They are used primarily for refractory cements and for high temperature precision molding of parts¹². The ability to accurately mold, finish, shape and reinforce these cements with various fibers also offers the added advantage of improving their formability and structural strength at high temperatures.

2.2.1 Calcium Aluminate Cement Composition

The approximate composition of these CA cements generally include the following oxides (see also figure-1):

OXIDE	CALCIUM ALUMINATE
SiO ₂	3-11 %
Al ₂ O ₃	33-44 %
CaO	35-44 %
Fe ₂ O ₃	4-12 %
FeO	0-10 %
C ₃ A	0-10 %
TiO ₂	0-2%
P ₂ O ₅	-
Mn ₂ O ₃	0-1%
MgO	0-.5%
Na ₂ O	0-.5%
K ₂ O	0-.3%

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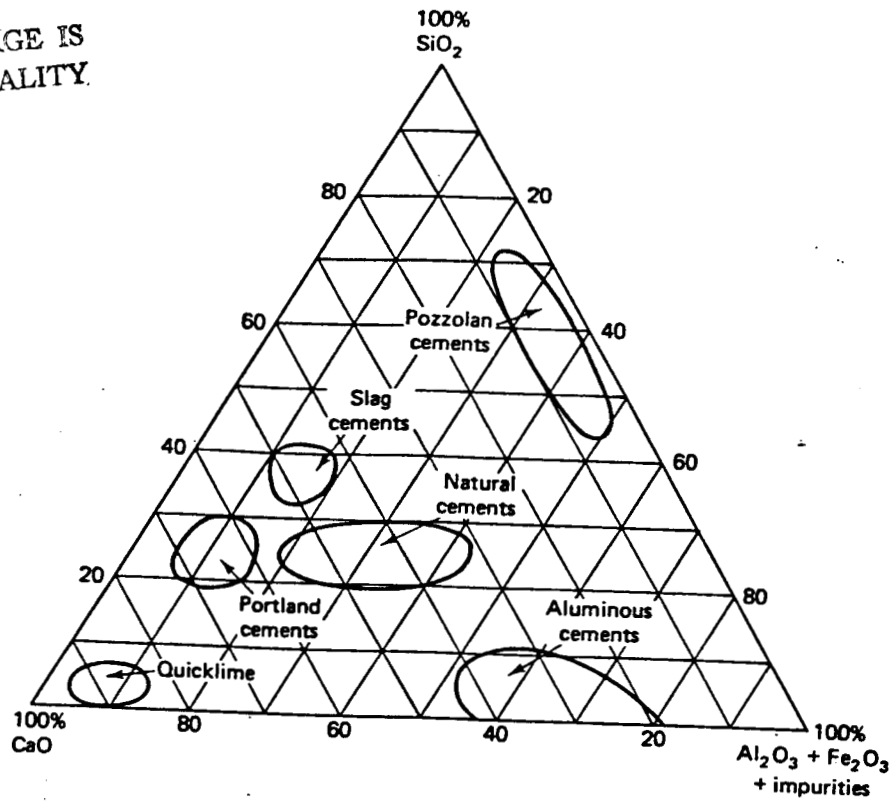


Figure-1
Approximate Composition of Various Cements by Weight

2.2.2 Manufacture of Calcium Aluminate

Calcium aluminate cements are generally made by fusing limestone and bauxite in an electric furnace. The kiln reactions for many of these basic materials were derived by Bogue¹³ based upon the known reaction sequence. These inorganic cements are usually formed and molded under hydration reactions or hydro-thermal reactions. These hydration reactions are much more complex and less understood than formation of the basic materials themselves.

These resulting calcium aluminate cements can withstand high temperatures. Other cements such as Strontium aluminate and barium aluminate cements withstand even higher temperatures. Commercially available cement materials of various compositions have been developed for the above mentioned electrical and thermal structural support applications and are readily available for the proposed spark wire and drift chamber applications.

ALCOA manufactures several calcium aluminate materials for casting and spray-up applications. ALCOA's CA-25 material commonly used for refractory cements was evaluated as part of the present study.

2.3 Reinforcement

Historical Development of Fiber Reinforced Cement

In the early development of fiber-reinforced concrete various forms of short pieces of steel were added to improve the mechanical properties of concretes. Two of the early investigators were Porter¹⁴ in 1910 and Graham¹⁵ in 1911 who advocated the addition of steel fibers to conventional reinforced concrete to increase the strength and stability; in 1914 Ficklin¹⁶ was granted a patent based on methods for improving the properties of concrete with steel fibers. Kleinlogel¹⁷ was issued a patent in 1920 covering the addition of small steel fibers to portland cement paste to form a material which could be a potential replacement for cast iron in many applications. Martin¹⁸ obtained a patent in 1927 for a method of forming concrete pipe reinforced with short steel fibers.

Etheridge¹⁹ was one of the first to investigate the effect of the shape of fibers on the properties of concrete. His patent of 1933 was based on the concept of using annular fibers of different sizes and shapes to improve the crack resistance and fatigue resistance of concrete. Another patent was issued to Zitrevic²⁰ in 1928 for the use of iron wires in concrete. In 1943 Constaninesco²¹ was granted a patent based on concrete reinforced with helical coil fibers, which has some characteristics similar to present fibers with aspect ratios of 100 to 300,

diameters between .035 (8.9×10^{-4} m) and .08 (20×10^{-4} m) inches and the concrete contained about 3.3 vol percent of fibers.

These and other early investigations and patents did little to increase the understanding of the mechanics of fiber reinforcement. In this respect, the investigations by Romauldi and co-workers²² in the 1960s are significant because they proposed a crack arrest mechanism to account for the improvement in the mechanical properties of concrete caused by the incorporation of steel fibers. This work led to patents based on fiber spacing assigned to Battelle Development Corporation in 1969 and 1970²³. Others started to investigate steel fiber-reinforced concretes and a patent based on bond and aspect ratio was granted to the U.S. Steel Corporation,²⁴ in 1972.

During the same period the use of glass fibers in hydraulic cements was studied by Biryukovich and co-workers^{25,26} in the U.S.S.R., by the Building Research Station^{27,28} in England and in the U.S. by the Corps of Engineers.^{29,30} Significant patents on alkali-resistant glass fibers^{31,32} and glass fiber-reinforced gypsum plaster³³ have been issued to the British National Research and Development Council based on investigations by the Building Research Station.

The interest in fiber-reinforced concrete has significantly increased in the past decade and a better understanding of the mechanics of fiber-reinforcement has been gained. Because of increased interest in and the realization of the potential of fiber-reinforced cementitious material for use in construction, symposia have been held in the U.S.^{34,35} and in England³⁶ devoted exclusively to these materials. Furthermore, a State-of-the-Art Report on Fiber Reinforced Concrete has been published by the American Concrete Institute,¹ and a technical report entitled, "Fibre-Reinforced Cement Composites" has been issued by the Concrete Society.³⁸ An excellent introduction to fiber-reinforced concrete has been given by Batson,³⁹ and Hoff⁴⁰ has briefly reviewed the developments of fiber-reinforced cements and concretes, covering the literature up to early 1974, and are available.^{1,41}

2.4 Glass Fibers

The present research has concentrated primarily on the use of glass fibers for cement reinforcement. This is because the application to spark chambers will require good electrical insulation and low organic outgassing.

Also, in an attempt to hold the large number of physical variables in the subsequent sample tests to a minimum, the type, alkaline resistant finish and size of the glass fibers were held constant throughout this study. Only the volume of fibers

was varied between different mixes.

2.4.1 Previous Research with Glass Fibers

Glass fibers have been extensively studied as cement reinforcing elements. Generally they are produced in the form of filaments which are combined to make strands, rovings, and woven to form chopped strands or mats. A typical glass strand consists of 200 to 400 single filaments of 10 mm diameter and a roving consists of 20 to 60 such strands. The major type of commercially available glass fibers are low-alkali borosilicate glass called "E-Glass". Type E glass fibers are generally degraded by the high alkalinity of hydrated portland cement and to a lesser degree by Calcium Aluminate cement. Therefore common commercially available glass fibers are not appropriate for use as reinforcement fibers for cements. The possibility of protecting E glass fibers from alkaline attack with organic coatings has been extensively investigated. Several generations of Alkali resistant glass fibers have been developed at the British Building Research Station and have been made commercially available. Majumdar²⁸ has however reported that some these treated fibers are slowly degraded by the alkalinity of Calcium Aluminate and to prevent this "fly ash" must be added to the cement.

Commercial manufacturers have developed improved chemical resistant fibers subsequent to Majumdar's tests. One notable material is Cem-Fil II⁴².

2.4.2 Glass Fiber Reinforcement Types

Glass fibers used as a cement reinforcement have been extensively studied within the past 15 years.

One of the promising candidate materials is treated glass fibers manufactured under the name of Cem-Fil-II. Glass fibers are less brittle than many high strength fibers. The strength, stiffness and price of glass reinforced cement lies between the corresponding values of asbestos cement and glass-reinforced plastics. The problem with commercially available glass fibers (E-glass), however, is that they are chemically attacked by the high alkaline environment of cement in its past stages and, as a result, the fibers lose part of their strength. The manufacturer of Cem-Fil II claims that this problem has been solved and early experiments tend to confirm this. This solution has been made possible by more alkali-resistant glasses with special compositions of the bulk glasses or by subjecting conventional "A" glasses or "E" glasses to surface diffusion treatments. Alkali-resistant glasses currently cost twice the price of ordinary glass fiber reinforcements.

2.4.3 Long-Term Performance of Alkali-Resistant GFRC

Since 1968 the use of alkali-resistant glass fibers for reinforcing cement has received applicable attention because of their excellent engineering properties. There has been concern primarily in high alkaline cements such as portland cement. High alumina cements such as Calcium Aluminate contain only small amounts of alkali. The most widely used glass fiber is a special alkali resistant material known as Cem-Fil-2. It is manufactured and marketed by Fiberglass Limited a member of the Pilkington group. This material is available in the form of chopped rovings or chopped strand in lengths from 12-50 mm. Generally the strength of the cement will increase as the length of the fibers increase.

2.5 Effect of Fibers In Cement

There are two classical methods generally used for fiber reinforcement of materials:

- (a) ductile fiber reinforcement of brittle materials
- (b) brittle fiber reinforcement of ductile materials such as polymers.

Fiber reinforcement of cements falls into the first category only because of the relative strength of the glass fibers compared to the cement matrix. The used of brittle fibers in ductile polymers will not be discussed as part of this project since this is the more classical fiber reinforcement technique used for plastics and epoxy systems.

Fiber reinforcement of cement materials does improve the tensile strength as well as in the post cracking strength and also provides an interface to absorb the "work of fracture," thereby improving the fracture toughness of these materials. Experiments have shown that the work of fracture in plain cement can be increased up to 40 times with glass fiber reinforcement of only 2% by volume ⁴³. This fact offers improvements in the range of tensile strains through which the material can go. This reinforcement also improves the impact resistance and the work of fracture. The selection of appropriate fiber types and arrangements can therefore be used to tailor make cement structures of specific strengths and ductility requirements.

This improved application of fiber reinforcement to cements provides:

1. increased resistance to brittle fracture, resistance to cracking and spalling;

2. increased resistance to thermal shock;
3. improved strength under abrasion and severe climatic conditions
4. material properties which permit design of thinner sections at faster production rates.

When the loads which are imposed upon concrete approach the matrix cement's allowable stress levels, cracks will propagate, sometimes rapidly. Fibers and inert fillers as well as voids resulting from pore water provide a means for arresting this crack growth. Similar to steel reinforcing in conventional portland cement, fibers provide a mechanism for supporting the tensile stress loads in the cement mix. Short discontinuous fibers have the advantage of being uniformly mixed and disbursed throughout the concrete. Common type of fibers include steel, glass, carbon, asbestos, polypropylene and polyamid.

In addition to the improvement in strength, ductility and fracture toughness, the addition of glass fibers to the cement mix also reduces the amount of shrinkage of cement product. For example, shrinkage of glass fiber reinforced cement is reduced 35% by the addition of only 1.5% fibers by volume⁷. Generally the addition of fibers does not improve the modulus of elasticity of the material.

A wide range of materials have been investigated as potential reinforcing fibers for cements, mortars and concretes, with the most common being steel, glass, organic polymers, carbon, and natural materials (asbestos, mineral wool and vegetation). References^{1,27,31-35} are particularly good sources for information on the typical physical properties of many of the commonly used fibers.

2.5.1 Effect on Flexural Strength

Glass fibers have been observed to increase the flexural and tensile strengths of portland cement pastes, calcium aluminate and concretes, and gypsum plasters, with maximum improvements being as much as four times that of the unreinforced materials. Such improvements were achieved when 8 wt %, of glass fibers were incorporated into gypsum and about 14 wt % were incorporated into portland cement and calcium aluminate cements.²⁷ The concentration of glass fibers is the important variable as the length of the glass fibers has little effect on the flexural and tensile strengths of the composites.

The effects of glass fibers on the moduli of elasticity of the various matrices covered in this review are generally slight. An example of enhanced modulus of elasticity is the reinforcement of a cement matrix with carbon fibers (unidirectional fiber array) in which the modulus of elasticity was increased

from 1.5×10^6 to 4.5×10^6 psi (10.0×10^3 to 30.0×10^3 MN/m²) by 8 vol %, of fibers.

2.5.2 Toughness

A measure of toughness of fiber-reinforced cements and concretes is the area under the complete tension or compression stress-strain curve, or the area under the load-deflection curve.

Johnson⁴⁶ has suggested that toughness based on load-deflection curves should be defined as the area under the curve up to the maximum flexural strength attained, or up to a specified deflection consistent with the cracking allowable in service.

Regardless of the method used to measure the toughness, the toughness of glass fiber-reinforced cements, are significantly higher than their unreinforced matrixes. For example, the toughness of fiber-reinforced concrete has been shown to be at least an order of magnitude, higher than unreinforced concrete, and to increase with increasing fiber content.

The impact strength of glass fiber-reinforced gypsum (about 12 wt % fiber content) has been reported to be between 20 to 30 times that of unreinforced gypsum and to be up to 5 times higher than that of asbestos fiber-reinforced gypsum³. Asbestos fibers, themselves, can double the impact resistance of cements when incorporated into the matrix at 10 to 11 wt %. Goldfein⁴⁸ studied the effect of many plastic fibers and found that nylon and poly-propylene fibers can increase the impact resistances of concretes by up to 30 times that of unreinforced concretes and,, in this respect,, are more effective than glass fibers.

However, Chan and Carlson⁴⁹ reported that fibers had little or no effect on the compressive strengths of concretes regardless of aggregate size, volume of fibers, or fiber length. Contradicting results have also been obtained with polymer-impregnated steel fiber-reinforced concretes. Steinberg et al⁵⁰ observed little gain in compressive strengths over impregnated concrete when 2 vol % of steel fibers was incorporated; while Flajsman⁵¹ et al reported that the compressive strength of a polymer-impregnated, fiber-reinforced mortar (2 vol % steel fibers) was twice the strength of an unreinforced polymer-impregnated mortar. (with glass fiber, Flajsman et al found a 50% increase in compressive strength).

2.6 Available Methods of Fabrication

Glass fiber reinforced cement (GFRC) can be formed in a number of ways:

- Casting or molding fiber/cement mix in a form

- extruding mix through a die
- Spray up of cement slurry with chopped fibers.

Fiber reinforced cements have been manufactured by a wide variety of each of these processes. However, one notable process is a good candidate system for use for manufacturing the spark wire frame or drift chamber frames construction. This method uses a simultaneous spray-up of low water content cement slurry and chopped fibers into a mold; then removal of excess moisture is accomplished by applying vacuum to a porous mold, and then finally by vacuum baking. This method was described by Biryukovich in Reference 52.

This construction method is a variation of the most commonly used method which uses a spray-up of the mixture in a multi-pass operation followed by rolling and then vacuum de-watering operation. Depending on the properties required, sand or inert filler is added to the cement. Pulverized flyash may also be added to minimize the alkaline attack of the fiber materials.

For the proposed spark wire frame application we would recommend the use GFRc sprayed in thin frame sections, a system of simultaneously spraying the chopped glass fibers and cementitious slurry on a flat surface or into a mold would be the preferred construction method.

The slurry is pumped to a nozzle where it is atomized by an air jet and mixed with the chopped Cem-Fil fibers en route to the casting surface. For sections which may have complex shapes, hand spray up techniques would be used. The spray operator aims to build up on a mold surface a layer of uniform thickness which is checked periodically with a depth gauge. Each layer is then consolidated by means of a disc roller to produce a neat smooth surface. This system is ideally suited to the fabrication of hollow sections and composite panels having lightweight core materials and void fillers.

For components that are mainly flat a mechanical spray-suction method is available. The cement slurry and glass fibers are sprayed together by means of a reciprocating spray head on to a moving conveyer thus producing a continuous "sheet" of GFRc. This material then passes over vacuum boxes situated to extract surplus water before the material moves under a device which compacts it and leaves a good flat finish. Finally the fresh composite is trimmed and cut to length before being handled by vacuum lifting pads and then either stacked as flat sheets, or shaped to form components. Because less water is used, this system produced GFRc of greater density and strength than that obtained by the hand spray process.

With a closely controlled mixing cycle to minimize damage to the glass fiber, conventional pre-mixing may be considered. The dry materials are mixed with water, preferably in a pan-type mixer, and the resultant mixture used to produce components by well established techniques such as injection, slip forming and vibration. The finished composite will tend to have random orientation of the fibers in three dimensions rather than in two when direct spraying is used. This means that the components made by the pre-mix process are likely to have a lower strength.

Whatever the method of manufacture careful moist curing must be applied to the fresh GFRC to prevent the relatively thin sections from drying prematurely.

2.7 Problems of Residual Water Removal

After full hydration has been completed, the end cement product contains from 10% to 25% by weight of chemically bound water which cannot be released by desiccation or heating. It does, however, contain around 15% by weight of "gel-water" absorbed in the cement's gel pores and capillary pore water in larger cavities in the order of 1,000 A wide. Both the gel water and capillary water can be completely removed by desiccate or by heating to 100°C at atmospheric pressure or by vacuum baking. Due to the volatility of gel water, desiccated cement contains about 25% by volume of gel pores of about 20 A. It should be pointed out that the water permeability of hardened cement is less than for most rock materials. This capillary pore volume is, however, the penalty paid for complete hydration.

2.8 Molding and Autoclaving

In the manufacture of cement products, autoclaved cements have produced compressive strengths of 20,000 psi. It is expected that elevated cure 120° F - 140° F of GFRC would produce relatively high flexural strengths. The proper selection of elevated cure temperatures and pressures is dependent upon the strength characteristics desired. Flexural strength in excess of 10,000 psi (70 MPa) have been achieved¹ using portland cement and alkali resistant glass fibers in pipe construction in England. With the strength of calcium aluminate cements expected to be twice that of portland cement it is therefore expected that sufficiently high flexural strengths can be developed using Cem-Fil-2 and calcium aluminate cement. Although experiments conducted by this SBIR project, to date, have not produced mixes which can achieve this strength

2.9 Mix Designs - Using Glass Fibers

At present, Cem-FIL is used in the form of chopped roving or chopped strands in lengths from 12-50 mm. Generally the strength

of the composite should increase as the fiber length increases but the longer fibers may create problems in the fresh state during some compaction processes.

In non-sprayed applications a shorter fiber helps to provide better flow characteristics and aids compactability when profiled units are being made.

The optimum quantity of fibers added for most production processes appears to be 5% by weight. For some application where careful orientation is achieved smaller quantities of fiber are adequate. For example in the manufacture of spun concrete pipes less than 1% by weight of glass fiber is added.

2.10 Matrix Mix Designs

The normal range of calcium aluminate cements can be used in GFRC manufacture and because it is necessary to minimize the drying shrinkage, quantities of fine sand (zone 4) or pfa are normally added. Generally the quantity of fines does not exceed that of the amount of cement used and the usual proportions are 60% cement and 40% fine material, sufficient water is added to suit the method of manufacture. Water reducers, accelerators, retarders and air-entraining admixtures are added when a particular property cannot be achieved without them.

2.11 Quality Control

Systems for quality control must be introduced into most production processes. These include the regular measurement of fiber and water content and the monitoring of strength and density.

Continuous checks on unit thicknesses during hand spraying work, particularly in sandwich type construction, are an important feature of production control.

2.12 Properties

The mechanical properties of GFRC depend upon a number of factors the most important of which are: orientation, length and quantity of glass fibers; constituents of the matrix; method of manufacture; curing conditions; age.

Because the fiber content is relative small the composition of the matrix controls: the compressive strength, elastic modulus, density, shrinkage, fatigue and creep behavior.

2.12.1 Tensile and Impact Strength

The effects of the environment and age do have a marked effect on the strength of GFRC's enhanced performance due

to pores lost with time. This loss is pronounced where the material is exposed to moist conditions.

However, when calcium aluminate is used in relatively dry air the materials should retain most of its mechanical properties in the long term. In normal outdoor conditions however GFRC tends to become brittle due to moisture degradation of the glass fibers.

2.12.2 Other Properties

Detailed studies of the properties of GFRC are now well documented, and some of the more important details are as follows.

Creep

At bending stresses below the LOP, i.e. at the normal working range of the material, the creep behavior of GFRC is virtually identical in general form to that of cement paste and sand/cement mortars. The elastic deformation is followed by a further slow creep deformation when the load is maintained, with the creep rate decreasing with time.

Fatigue

Repeated load fatigue tests on spray-dewatered GFRC have produced a common form of S-N curve. Bending tests have given fatigue life greater than 10^5 cycles at the LOP stress level, and greater than 10^5 cycles at the normal flexural working stress levels.

Density

The incorporation of glass fiber leads to some air entrainment and reduction in density. For standard composites containing the normal 5% by weight of glass and up to about 25% by weight of sand the density of the spray-dewatered GFRC is usually in the range of 2 to 2.2 tons per m^3 and for non-dewatered material the density is a little lower in the range of 1.7 to 2.1 tons per m^3 .

Shrinkage

As with other cementitious materials GFRC undergoes drying shrinkage on exposure to low humidity/high temperature conditions. For material with a calcium aluminate cement matrix the ultimate drying shrinkage can be up to 0.3%. In a mix with sand cement ratio of 0.5:1 the ultimate shrinkage can be reduced to around 0.15%.

Thermal Expansion

Between 7 to 12 x 10⁻⁵/°C for dry material.

Thermal Conductivity

Between 0.5 W/mK at 1.7 tons per m³ to 1.3 W/mK at 2.2 tons per m³.

Fire Resistance

GFRC materials have been classified as non-combustible and not easily ignitable.

2.13 Commercial Applications

Glass fibers are now being used in continuous filament form to reinforce concrete rather than just cement and fine aggregate mixtures. By carefully locating the fiber it is possible to replace conventional steel reinforcement. The manufacture of precast pipes is an example of this usage.

One of the first commercial applications of GFRC to emerge, was in the field of cladding. Single skin and sandwich type panels with lightweight cores have been used with a variety of shapes and finishes.

The recent imposed bans on the use and handling of asbestos has created a void in the asbestos reinforced concrete industry.

The use of glass fibers to reinforce cement products can satisfy this need. This would include structural paneling and pipe materials to replace transite type materials.

2.14 Recent Developments in Fiber Improvement

The need to improve the long term performance of glass fibers in a cementitious matrix, has prompted Pilkington Bros to devote some considerable effort towards producing a more durable fiber. It is now claimed that this has been achieved and

recently the availability of Cem-FIL 2 was announced. This new fiber receives some special treatment during manufacture which, it is claimed, improves its resistance to any deleterious reaction with the cement matrix. The resultant composite can thus retain more of its initial strength properties.

3.0 Test Program Conducted as Part of This Research Project

3.1 General:

As part of the present project, a series of samples were obtained from commercial manufacturers of refractory cements. These materials were made in batch lots and tested to verify the effects of adding reinforcement materials to improve the strength of the commercially available materials.

The materials used were in general refractory cements with a calcium aluminate base and inert silica filler materials added. In a subsequent series of tests, the basic materials were obtained and mixed in various proportions to determine their properties and variations in their properties with changes in the mix designs.

3.2 Calcium Aluminate Cement

The material used for these experiments was ALCOA's CA25 calcium aluminate casting cement. The "cut sheet" for this material is attached as appendix B to this report.

3.3 Fiber Properties

The Cem-Fil-II glass fibers used in this investigation were cut from strands in 1/2 in. (12 mm) length. They were supplied by the Glass-Coat Corporation of Florida under license Fiberglass Ltd. Glass. The glass fibers generally had the following characteristics

Diameter: 10-15 μm
Specific Gravity 2.6
Failure strain 3.5%
Modulus of Elasticity 80 GPa (11.6×10^6 psi)
Tensile strength 2-3 GPa (400,000 500,000 psi)

3.4 Mixing Procedure

Two main mixing methods were followed in this study: pre-mixing the fibers with the cement and fillers adding water to form a mortar matrix and the second used a premixed mortar to impregnate a mat of fibers.

In the premixing method, the non-fiber components (cement, sand, water and) were mixed first using a sufficient proportion of water to render the fresh mix liquid-like. Then the fibers were slowly added until the mix lost most of its fluidity. The remaining fibers and water were then slowly added trying to keep

a balance between harsh mix, fiber content and water content. The quantity of water required varied as a function of the mesh size of the inert filler used for the specimens. As the amount of very fine filler increased, (i.e. 140 mesh material) the quantity of water increased to prevent a dry mix.

The process and mix balance was extremely tricky since the resulting cement slurry was often thixotropic and would appear dry until vibrated. Often then a sequence of mixing and vibrating had to be used to minimize the amount of water used.

This procedure was mostly necessary when the total volume content of fibers was relatively large while the water content was relatively small. An additional mixing element was found to be important in this investigation and is described as the "apparent or bulk volume" of the fibers in relation to the volume of mortar. The "apparent volume" of the fibers can be described as the column they occupy if they are placed by dispersing in a container. It is substantially different from the "solid volume" of fibers. The apparent volume is related not only to the fiber packing but also to their shape, diameter and length. The shape of the fiber itself may be such that it entraps air, hence occupying a larger volume than theoretically predicted.

Another method of obtaining the calcium aluminate fiberglass composite (different from the above integrated method) was also used in this project. It can be described as the "impregnation" method. In this method a fiber matrix using the desired amount of fibers were weighed and preplaced in a mold and the premixed mortar matrix is then applied, accompanied by vibration to insure a better penetration. The advantage of this technique was that the mortar or paste can be optimally designed independently of the fiber type and content. Disadvantages included a higher probability of entrapping air resulting large voids in the samples which destroyed these samples. This last problem combined and the tendency of the slurry to plug up the mat or the mat to float during vibration, required better control of sample fabrication.

3.5. Mortar Mixes

Sixteen different mortar mixes were used in this investigation. Similar mixes were used with and without fiber reinforcements, and with different cure cycles. They are described in Table 1. The richer cement mixes had a smaller proportion of fine sand (all passing ASTM sieve No. 40 and 130). It was designed to achieve mostly a high first cracking strength. A superplasticizer was not used to increase fluidity during mixing, since it was felt that the nature of the subsequent outgassing could be a problem. In most series of tests involving high volume fractions of fibers, all components were pre-weighed dry mixed and then rapidly mixed and molded. This kept the mix

as workable as possible for the time period needed to prepare the specimens during the hydration reaction.

3.6 Forming - Fabrication

Specimens were poured into 1 1/2" diameter PVC pipe sections cut to length to form molds. Mixed lot batches were prepared from which specimens of dimensions 1-1/2" x 8" long were later cut for testing. All flexural specimens had the same dimensions.

The molds were vibrated with a mechanical vibrator screeded and rodded to simulate the possible production of manufactured pieces by applying a high level of vibration and compaction. The procedure seems promising and the composite obtained is only limited by the amount of fibers that can practically be premixed-

The resulting samples were then pressed into the molds and de-watered. Similar procedures were also used in combination with a pre-placed fiber mat and impregnated by a mortar matrix. Provided the mat has the proper characteristics, the procedure did offer molding difficulties. In addition, the composites obtained from the mat did not (in general) show better properties than that obtained by premixing and many of the samples were lost to large voids.

In the first set of specimens, all specimens were generally taken off the molds 24 hours after pouring and kept at 100% relative humidity and 72° for one week to one month before removal and testing. In a second set of specimens, the curing temperature was maintained at 120-130 ° F for the full cure cycle. This had a slight improvement in the strength properties.

3.7 Testing Procedure

All testing was performed using a hydraulic compression test machine. The loading head was attached to Lebow load cell and digital read out system. Deflection gauges were used to measure sample deflections. Both flexure and compression tests were conducted. For the flexural beams a three-point loading arrangement with an 8 in. span. The rate of stroke was 0.5 in/min. The load-deflection response was automatically plotted on an x-y recorder. The beams were generally loaded to failure or 0.5 in. deflection whichever occurred first.

3.8 Test Results

Table 2 attached shows the summary of flexural stresses and compressive stresses obtained for each of the mixes prepared. The results of the study were discussed with representatives of ALCOA, The U.S. Bureau of Standards, the Canadian Research Council to determine appropriate values for test levels.

As can be seen from Table 2, the maximum modulus of rupture obtained is near 5600 psi. Although some single samples were higher, no appreciable increase was observed for this material. Discussions with Dr. M. Zur of ALCOA's Pittsburgh refractory materials research group indicated the need for increasing the temperatures of cure. Unfortunately the time for preparing samples and testing did not permit a 28 day cure cycle to be completed before the required due date for submittal of this report.

The typical plots showing the relation of modulus of rupture to limits of proportionality are shown in Figures 2 and 3 attached.

4.0. Summary and Conclusions

The results of this SBIR investigation have developed the following conclusions and recommendations:

1. The use of calcium aluminate glass fiber reinforced cement presents the potential for improved fabricability of large spark wire and drift chamber frames. The material properties reported in the literature would indicate that the properties approach the strengths of ceramic materials previously used without the fracture sensitivity of ceramics.
2. The use of calcium aluminate should produce flexural strengths well in excess of 10,000 psi and probably close to 15000 psi minimum. However, the limited number of tests conducted as part of the present research showed nominal strengths between 5000 to 8000 psi. The large number of variables encountered during the performance of the test program coupled with the extended times required to cure samples protracted the test phase of this project well beyond the expected time frame. As a result additional samples will have to be made using other design mixes and cure temperatures to verify the purported strength requirements.
3. There is also a need to evaluate the long term creep and long term strength degradation properties of the CEM-Fil-II materials combined with the Calcium Aluminate materials available.
4. There is a need to develop an assembly procedure specifically for the spark wire frame fabrication using a "spray-Up" system and de-watering system to evaluate the problems associated with this process and to evaluate the resulting assembly problems for a full spark wire frame.

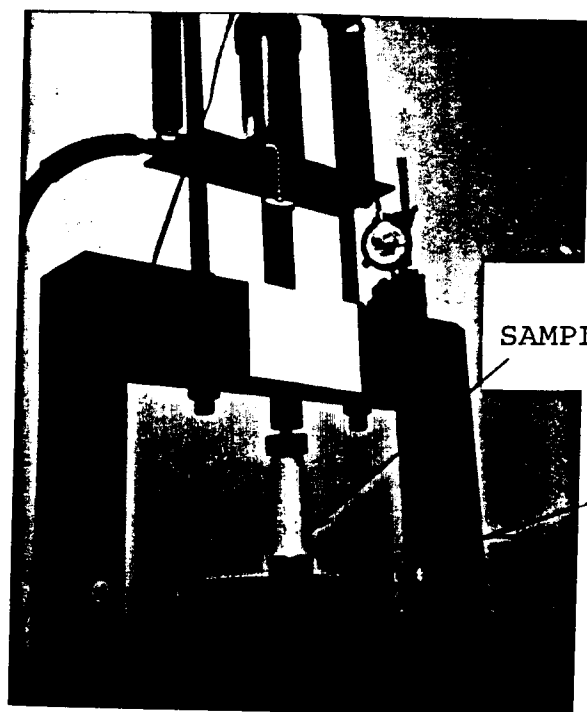
TABLE - 1
DESIGN OF MIXES USED IN TESTING PROGRAM

MIX NO.	CEMENT CA-25 %	INERT FILLER USED BY MESH SIZE %			WATER USED %	GLASS FIBERS %	CURE TEMP C
		30	140	300			
1	48	32	0	0	20	0	20
2	40	25	0	0	17	18	20
3	80	0	0	0	20	0	20
4	46	32	0	0	22	0	20
5	42	32	0	0	22	4	20
6	22	70	0	0	6	2	20
7	22	68	0	0	8	2	20
8	26	40	0	20	10	4	20
9	22	17	0	50	8	3	20
10	21	50	0	16	10	3	20
11	19	0	60	0	19	2	20
12	40	40	0	0	20	0	20
13	48	32	0	0	17	3	20
14	50	33	0	0	17	0	20
15	22	43	20	0	9	6	20
16	40	19	20	0	15	6	20
17	48	32	0	0	20	0	55
18	40	25	0	0	17	18	55
19	80	0	0	0	20	0	55
20	46	32	0	0	22	0	55
21	42	32	0	0	22	4	55
22	22	70	0	0	6	2	55
23	22	68	0	0	8	2	55
24	26	40	0	20	10	4	55
25	22	17	0	50	8	3	55
26	21	50	0	16	10	3	55
27	19	0	60	0	19	2	55
28	40	40	0	0	20	0	55
29	48	32	0	0	17	3	55
30	50	33	0	0	17	0	55
31	22	43	20	0	9	6	55
32	40	19	20	0	15	6	55
33	SA29-8	**	**	**	20.00	0.00	20
34	SA29-7	**	**	**	19.00	3.00	20
35	SA30-7	**	**	**	19.00	3.00	20
36	SA30-8	**	**	**	20.00	0.00	20
37	SA31-7	**	**	**	19.00	3.00	20
38	SA31-7	**	**	**	20.00	0.00	20
39	SA75-7	**	**	**	19.00	3.00	20
40	SA75-7	**	**	**	20.00	0.00	20

NOTES:

- * COMMERCIAL CEMENTS USED AS RECOMMENDED
- ** TYPE AND DISTRIBUTION OF FINES WERE AS RECEIVED AS A COMMERCIAL PRODUCT.

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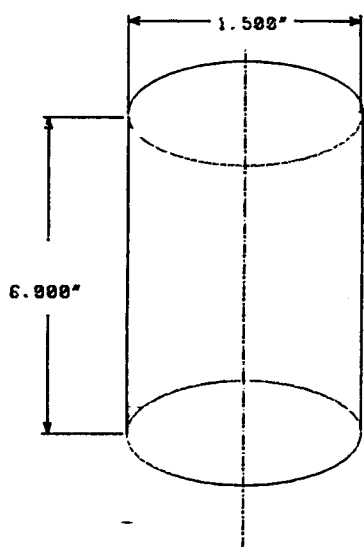


SAMPLE

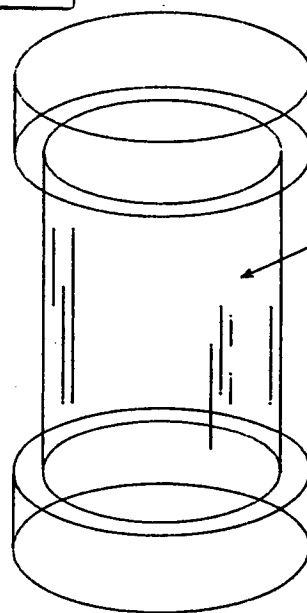
LOAD FRAME

Load

APPLIED LOAD



TEST SAMPLE



LOADING HEAD

SAMPLE

TEST SET-UP

FIGURE-2

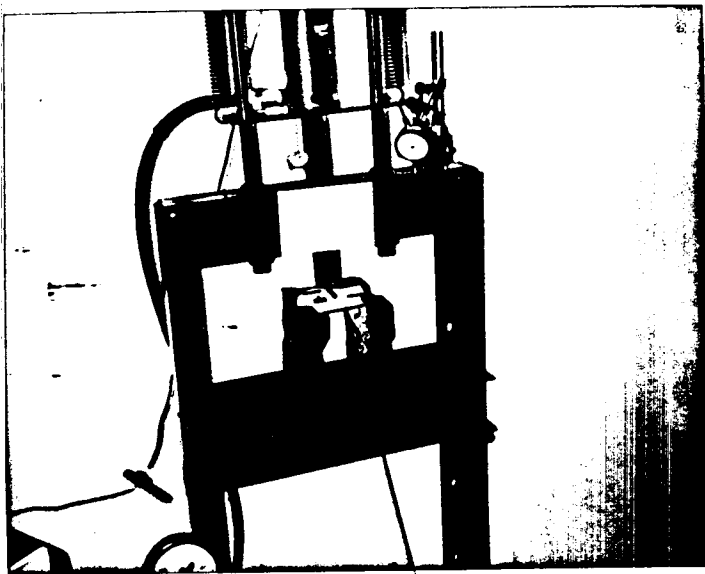
COMPRESSION TEST SET-UP

MEGA ENGINEERING
SILVER SPRING MARYLAND

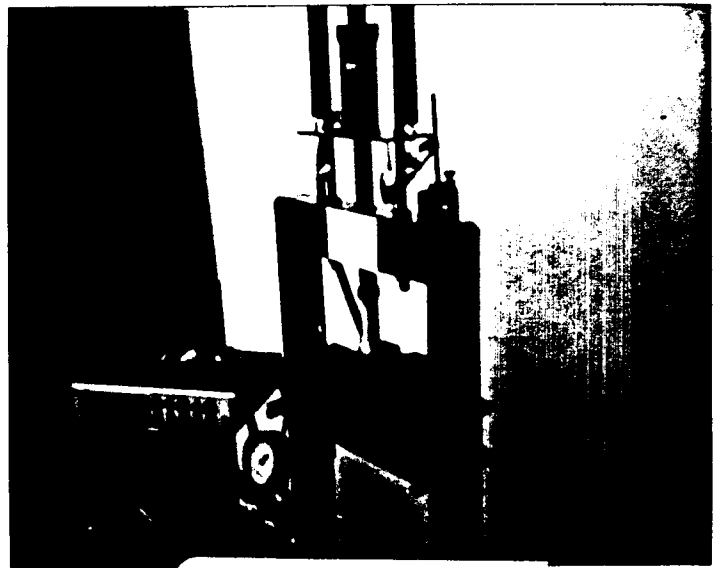
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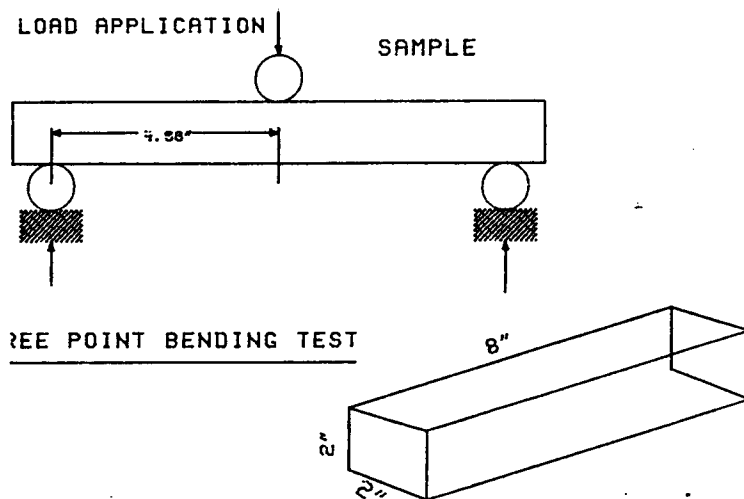
B-



BENDING
TEST SAMPLE



TEST & RECORD
SET-UP



FLEXURAL TEST SAMPLE

FIGURE - 3

THREE POINT FLEXURAL LOAD TEST SET UP

MEGA ENGINEERING
SILVER SPRING MARYLAND

13-

TABLE - 2
MODULUS OF RUPTURE AND COMPRESSIVE STRENGTHS
BASED UPON 8 SPECIMENS PER SAMPLE LOT

MIX NO.	CEMENT CA-5 %	WATER USED %	GLASS FIBER %	CURE TEMP C	MODULUS OF RUPTURE PSI *	COMPRESSIVE STRESS PSI *
1	48	20	0	20	1080	4000
2	40	17	18	20	5800	7600
3	80	20	0	20	480	2800
4	46	22	0	20	1800	4500
5	42	22	4	20	3600	7300
6	22	6	2	20	2600	3000
7	22	8	2	20	1800	2600
8	26	10	4	20	2100	3300
9	22	8	3	20	1200	1800
10	21	10	3	20	1400	2800
11	19	19	2	20	2200	2600
12	40	20	0	20	1200	4000
13	48	17	3	20	5800	8500
14	50	17	0	20	1500	7500
15	22	9	6	20	1600	2900
16	40	15	6	20	6200	9800
17	48	20	0	55	1600	5900
18	40	17	18	55	6100	8300
19	80	20	0	55	600	3300
20	46	22	0	55	2800	5100
21	42	22	4	55	5600	8600
22	22	6	2	55	2500	3100
23	22	8	2	55	2000	2700
24	26	10	4	55	2100	3700
25	22	8	3	55	1600	2300
26	21	10	3	55	1800	2100
27	19	19	2	55	780	1800
28	40	20	0	55	1400	4900
29	48	17	3	55	1600	9100
30	50	17	0	55	2100	7800
31	22	9	6	55	1600	3900
32	40	15	6	55	5800	9400
33	SA29-8	20	0	20	500	3500
34	SA29-7	19	3	20	1800	3200
35	SA30-7	19	3	20	300	4400
36	SA30-8	20	0	20	2000	4200
37	SA31-7	19	3	20	400	2200
38	SA31-7	20	0	20	1200	2100
39	SA75-7	19	3	20	325	3000
40	SA75-7	20	0	20	1200	3100

NOTES:
* ALL STRESSES ARE MEAN STRESS VALUES ROUNDED TO NEAREST 100 psi

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